



Microchemical and Gaseous Sensors Using Carbon Nanotubes and MEMS Fabrication Technology

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This research is a joint effort between the researchers in the Electronics Design Center at Case Western Reserve University and the National Center of Microgravity Research (NCMR)/Universities Space Research Association at NASA Glenn Research Center. The overall objective is to advance nanosensor technology for gaseous detection in propulsion and power systems for aerospace applications. The underpinning technology of this research is a combination of silicon-based microfabrication and micromachining processes and carbon nanotube technology.

In this research, photolithography and thin film metallization techniques were used to produce the basic sensor structure. This metallic sensor structure also served as the catalytic precursor for the formation of carbon nanotubes. Metals such as Fe, Ni and Co were the candidates for the catalytic precursor. An ion beam sputtering system was used to carry out the metallic thin film deposition.

Even though the grant started late and both research groups had delays due to laboratory renovation and equipment modifications, we have made excellent progress towards our research goals in the first year and second year. Specifically, we have carried out the following tasks successfully:

1. We identified nickel and cobalt to be the metallic catalysts appropriate for CNT synthesis. Accordingly sputtering targets for these metals were acquired. Different metal screen meshes and foils were used as the substrates for the deposition to test the suitability of these catalysts. The thickness of the deposition varied, including 5, 10, and 20 nm.
2. Polished quartz discs were chosen as potential sensor substrates for the study. The disc was approximately 1 cm in diameter and finely polished. Two types of metallic depositions were carried out. In the first type of deposition, the whole surface area of the disc was covered with deposited metal. Pure nickel and pure copper were deposited by the sputtering technique. A thickness of 20 nm pure nickel deposited on the top surface of 20 nm pure copper of a quartz disc was also undertaken. These deposited metallic films were then used as the sites for the growth of carbon nanotubes were then assessed.

The second type of deposition was carried out on patterned sensor structures on a quartz disc. Figure 1 shows the design of the sensor structure that has an interdigitated configuration. The design structure was then deposited onto 1 cm diameter quartz discs. Cobalt in the thickness of 5, 10 and 20 nm were deposited using a shadow mask. These structures are planned to be used for the growth of carbon nanotubes. The carbon nanotube covered sensor structures will then be ready for evaluation as a gaseous sensor.

3. Silicon carbide is a high temperature electric material. It has been considered as a potential sensor material that may be used in high temperature hazardous environments. In our study, the growth of carbon nanotubes on silicon carbide substrates was also countertubes. The process is a combination of catalyst reduction and carbon nanotube synthesis conditions. The characterization of the growth density and the uniformity arrayed SiC fibers supporting carbon nanotubes upon SiC are shown in Figs. 2 to 4 respectively.

Stainless steel mesh deposited with metal catalyst for the growth of carbon nanotubes were also carried out in order to test CVD or flame synthesis conditions. We may point out that the flame process is unique in the growth of carbon nanotubes. Figure 5 shows the results obtained. Figure 6 shows the coated quartz disc using chemical vapor deposition also. The results are not very good indicating a relatively poor combination of CVD and catalyst choice. Choice of catalyst and synthesis conditions matter!

Modifications on the experimental conditions were undertaken. Figure 7 and 8 shows the foundation of carbon nanotubes upon SiC, under modification, are more favorable. Figures 9 and 10 show the foundation of carbon nanotubes on stainless steel mesh under modified synthesis conditions. Figure 11 shows the growth of carbon nanotubes on a nickel-covered copper foil to explore synergy with sensor contacts. This was done using the flame-based synthesis technique.

The following images represent the best combination of catalyst, support and CNT growth conditions. Therein they should not be compared to each other for judging the relative merits of these parameters. The number of images, corresponding to the below conditions are presented in the report in order to illustrate the variety of final products that we have successfully synthesized to-date. Therefore, there are some specific points to be made regarding each sample. These are succinctly made in the caption for each figure.

Combinations of conditions that did not work are generally not shown in this report, with the exception of Fig. 6. This image is rather representative of all that did not work as such tests usually resulted in few if any CNTs upon a rather barren substrate.

To capture the synthesis tests conducted to-date, we have found our flame synthesis process to be optimum for catalysts (Co for now) supported on SS mesh. There is a small range of flame equivalence ratios that lead to excellent CNT growth (as judged by uniformity of diameter, lengths, areal density). The optimum catalyst for SiC fiber is either Ni or a Ni/Cu mixture. The best synthesis vehicle is thermal CVD using the mixture as indicated for sample no. 6.

Sample	Material	Catalyst	Treatment Reduction/Growth
1 (Fig. 2)	SiC fibers	Fe/Cr/Ni/Mn mixture	R & G1
2 (Fig. 3)	SiC fibers	Cu	R & G2
3 (Fig. 4)	SiC fibers	Cu	R & G2
4 (Fig. 5)	400 SS mesh	Co, 1.0 nm	R & G2
5 (Fig. 6)	Quartz	Cu, 25 nm	R & G2
6 (Fig. 7)	SiC fibers	Cu/Ni mixture	R & G2
7 (Fig. 8)	SiC fibers	Ni	R & G2
8 (Fig. 9)	400 SS mesh	Co, 1.0 nm	G3; $\phi = 1.62$
9 (Fig. 10)	400 SS mesh	Co, 1.0 nm	G3; $\phi = 1.80$
10 (Fig. 11)	Cu foil	Ni, 1 nm	G3; $\phi = 1.62$

Notes:

- G1 corresponds to a C₂H₂, H₂, He environment for CVD
- G2 corresponds to a C₂H₂/H₂/He + benzene gas mixture for CVD
- G3 corresponds to our flame synthesis, using primarily a fuel-rich mixture producing post-flame gases, of which the primary components are CO, H₂, H₂O and CO₂
- Here ϕ corresponds to the fuel/air equivalence ratio (note that $\phi > 1$ corresponds to fuel-rich conditions, i.e. incomplete combustion.)

These experimental results devised directly from a combination of carbon nanotubes and microfabrication techniques. Preliminary results provide guidance for the selection of synthesis conditions for the carbon nanotubes on a defined sensor structure. We anticipate substantial results will be derived in the forthcoming years.

Because of the issues involved in the laboratory renovation and the equipment maintenance, we have altered some of our research goals in the first and second years. In summary, we have done substantial research on the growth of carbon nanotubes on SiC. Also, the design and fabrication on the sensor structure (originally planned for the second year) have been moved forward and undertaken in this year. We made adjustments in order to maximize our research efforts.

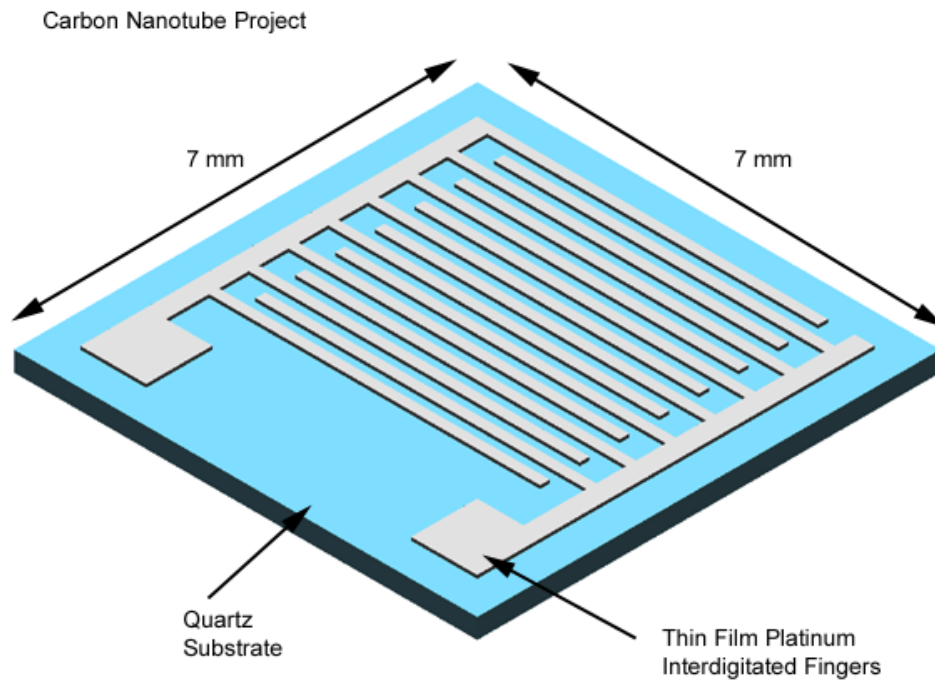


Figure 1. Configuration of the interdigitated sensor structure on which carbon nanotubes will be grown.

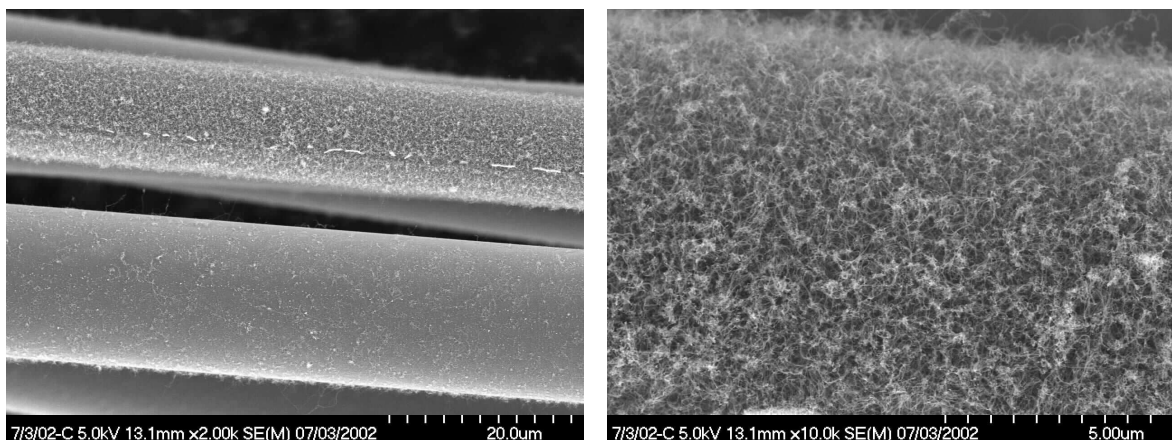


Figure 2. Carbon nanotubes upon SiC showing initial variability in the CVD processing.

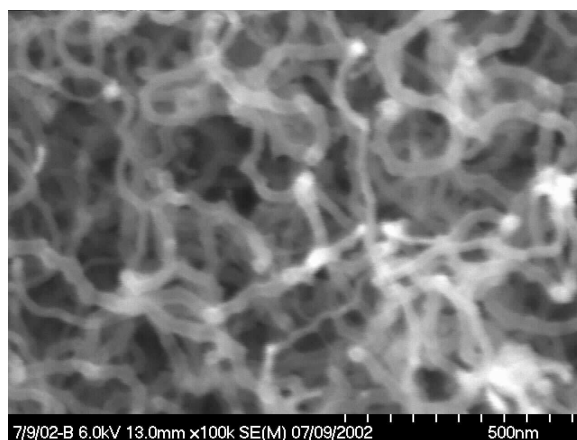
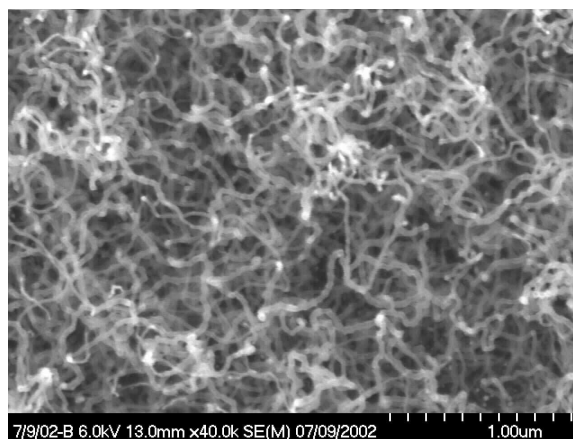
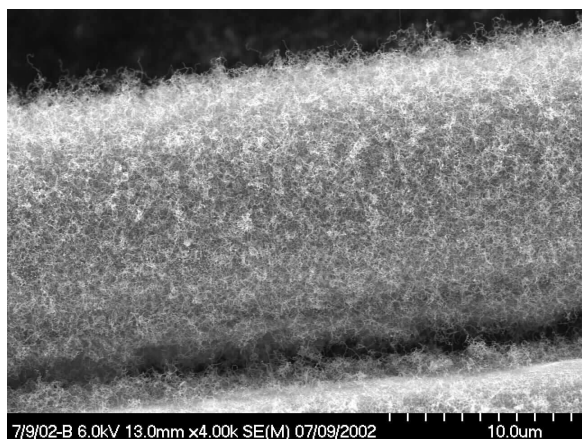


Figure 3. Carbon nanotubes upon SiC illustrating the density of growth.

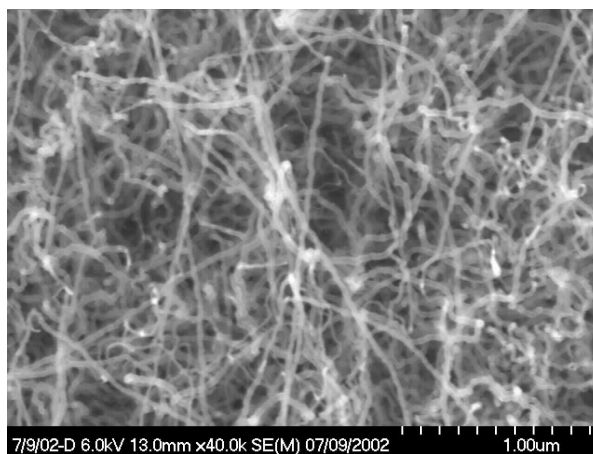
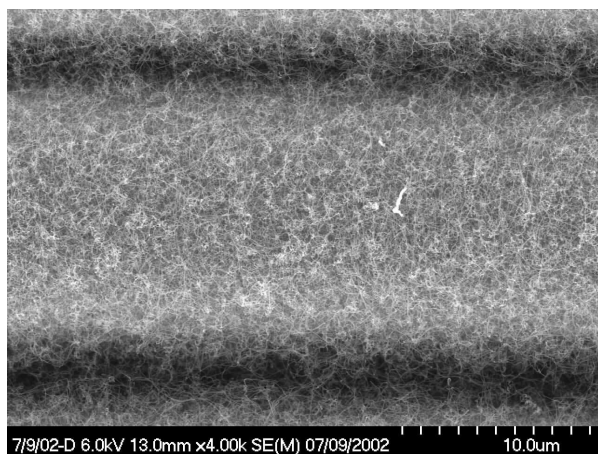
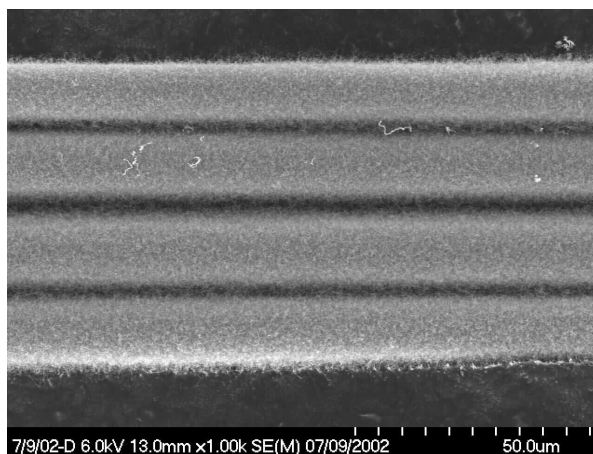
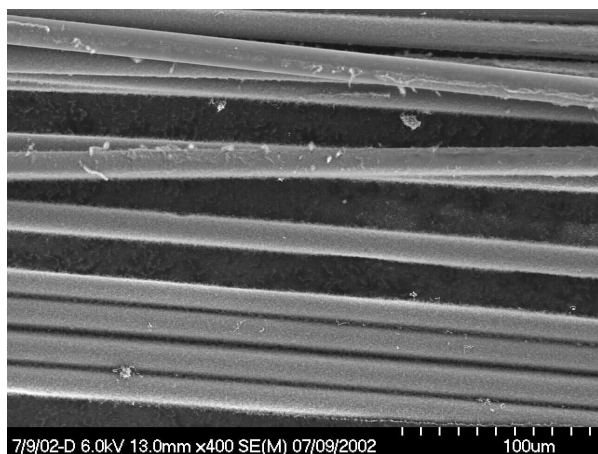


Figure 4. Uniformly arrayed SiC fibers supporting carbon nanotubes upon SiC.

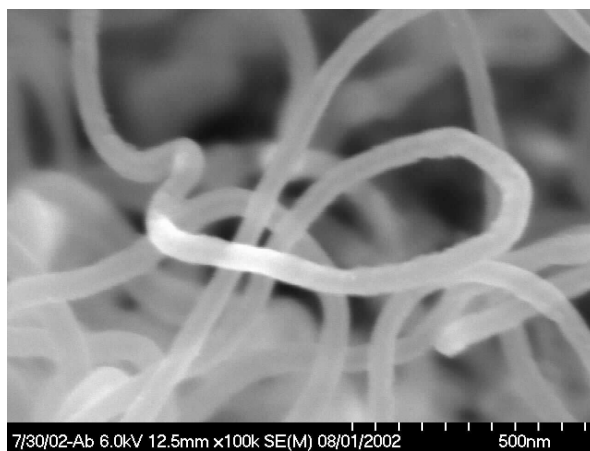
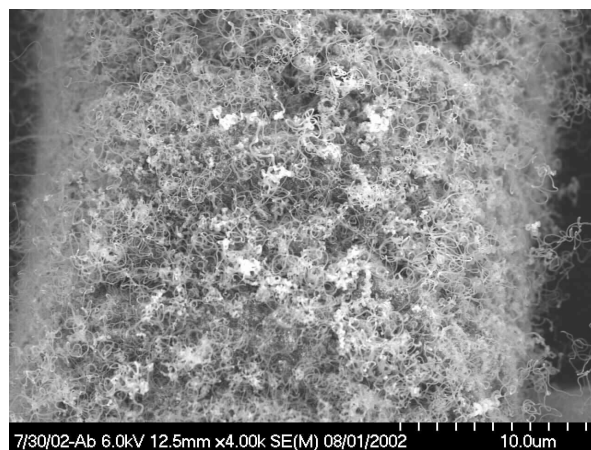
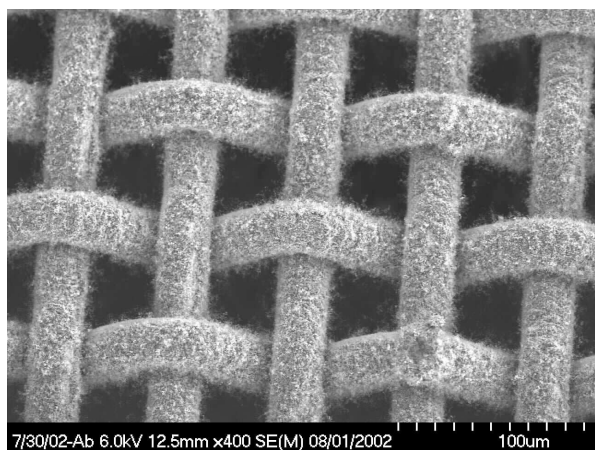


Figure 5. Carbon nanotubes upon SS mesh for identifying CVD and catalyst combinations.

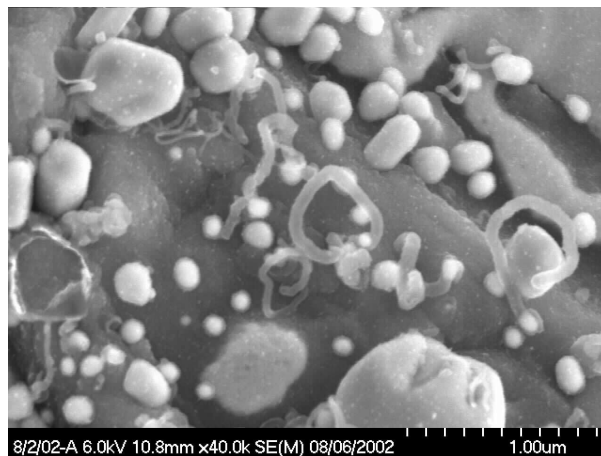
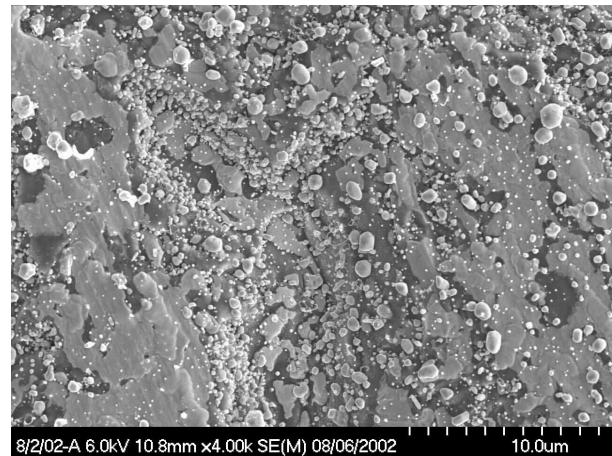
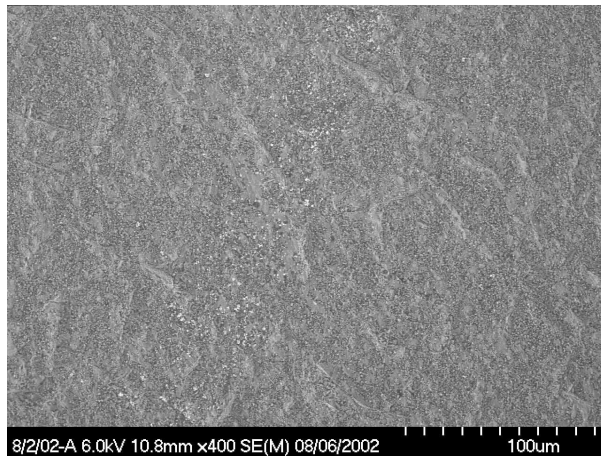


Figure 6. Carbon nanotubes Cu coated quartz illustrating a poor combination of CVD and catalyst choice.

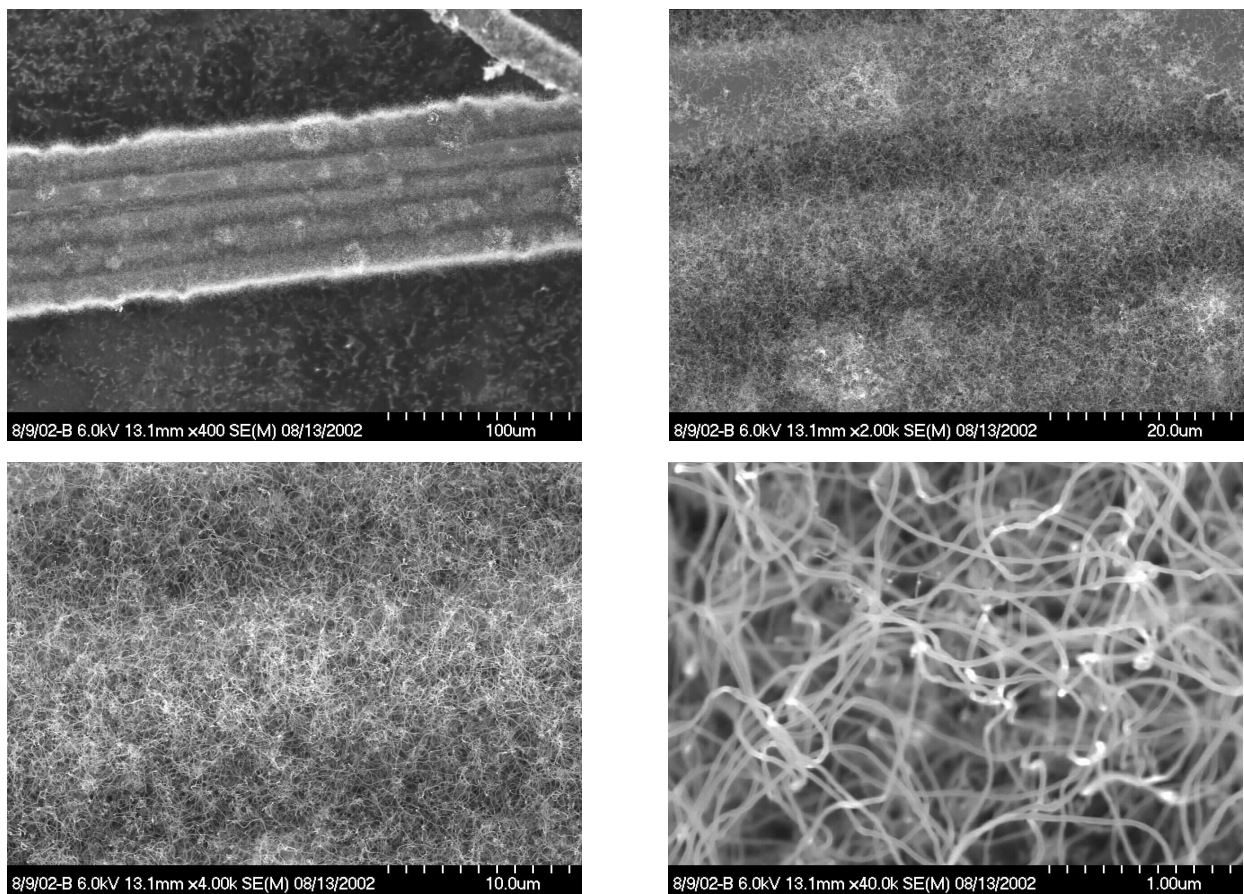


Figure 7. Carbon nanotubes upon SiC using optimum synthesis conditions.

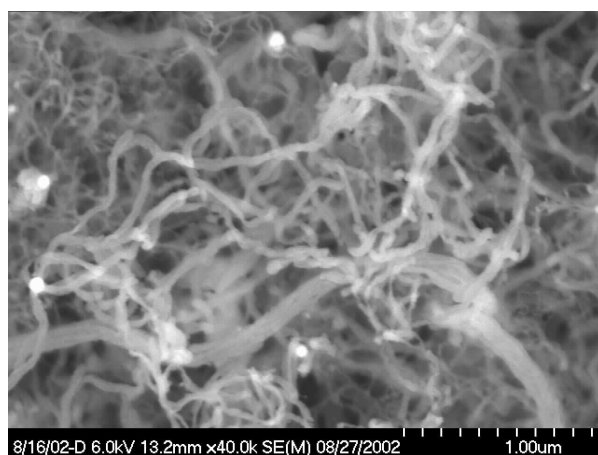
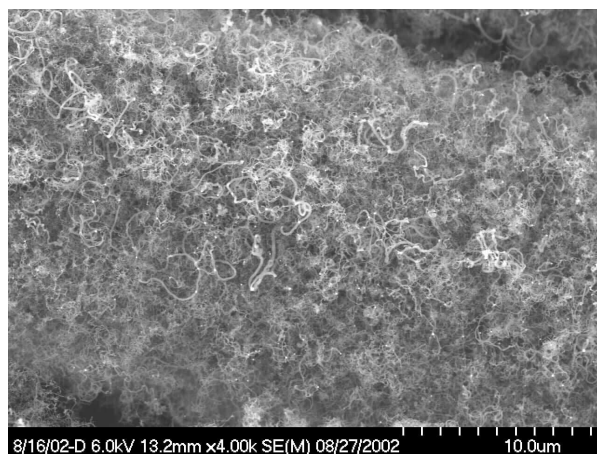
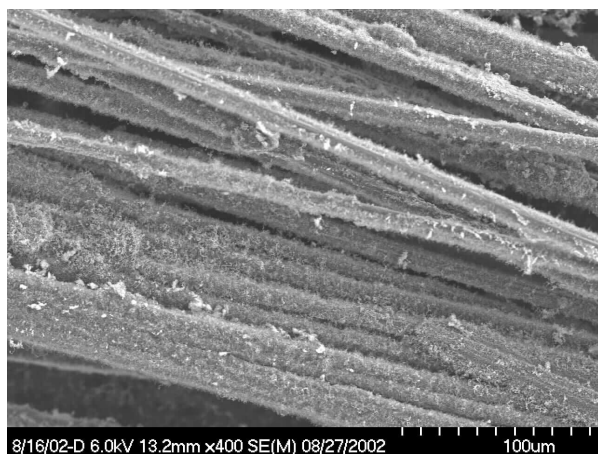


Figure 8. Carbon nanotubes upon bundled tow of SiC.

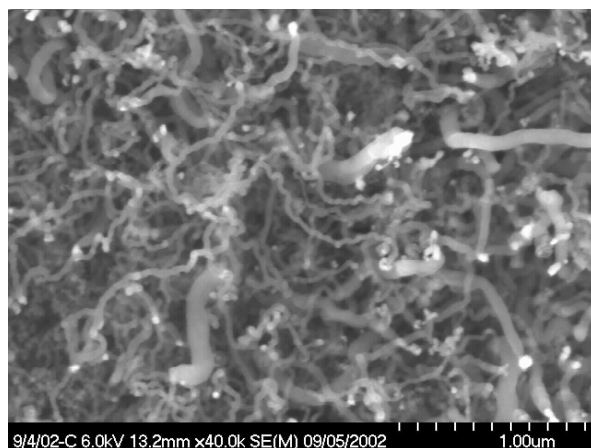
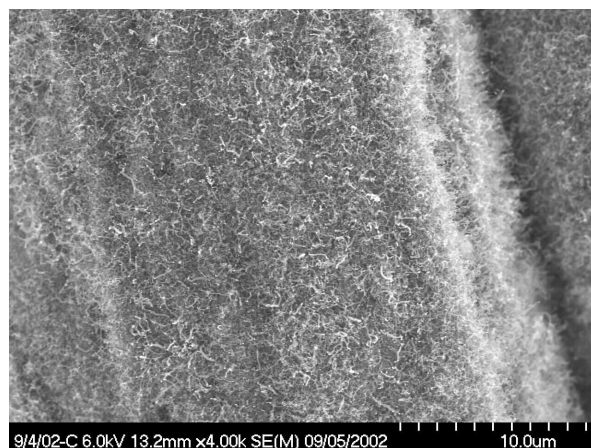
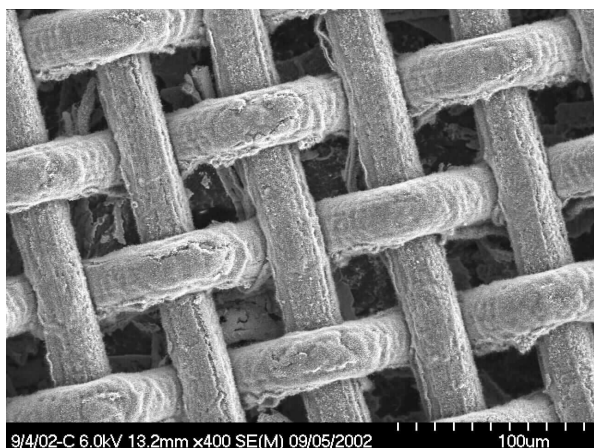


Figure 9. Carbon nanotubes upon SS mesh to guide synthesis conditions for CNTs.

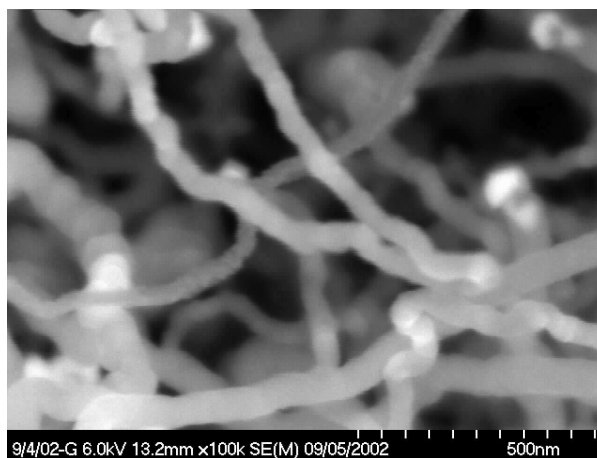
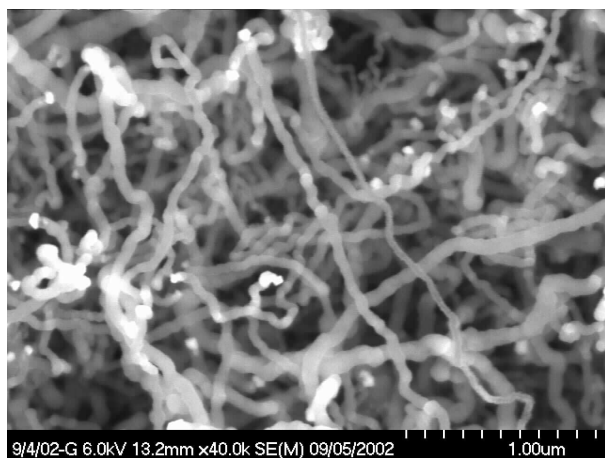
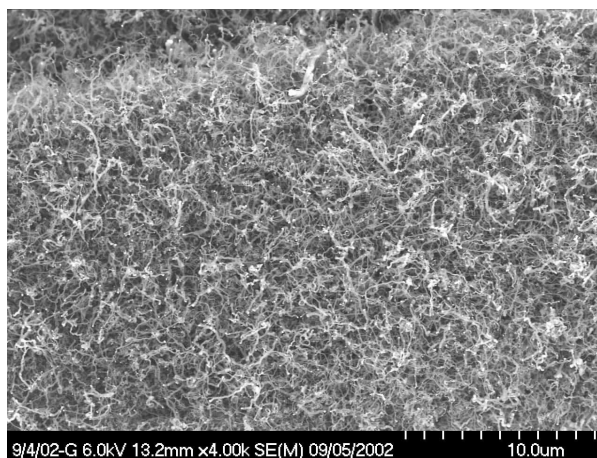
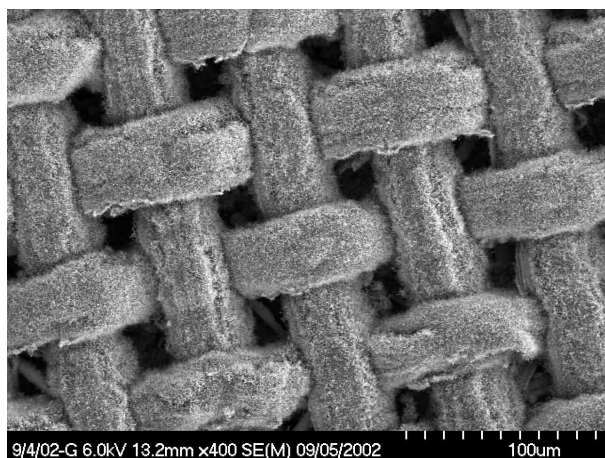


Figure 10. CNTs upon SS mesh under optimum synthesis conditions.

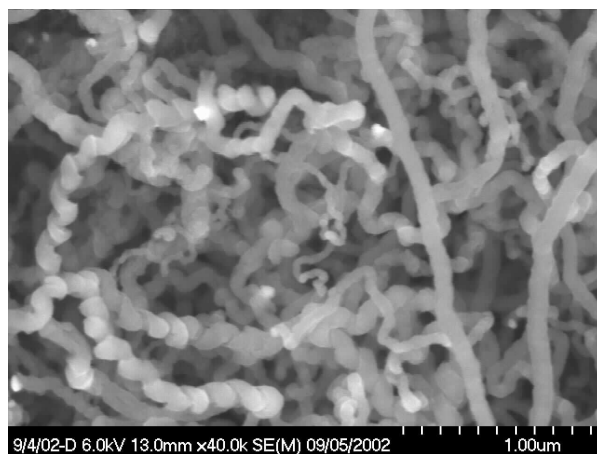
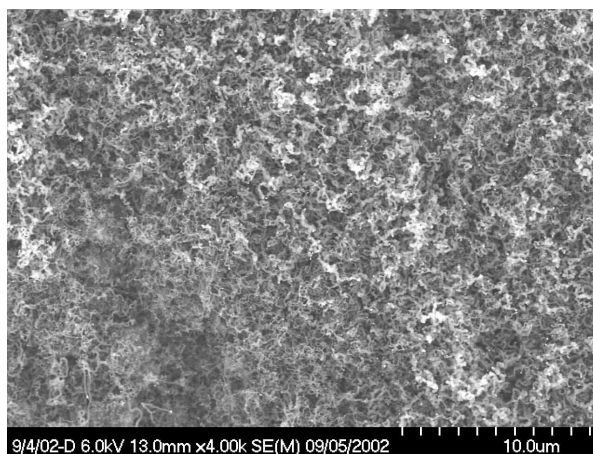
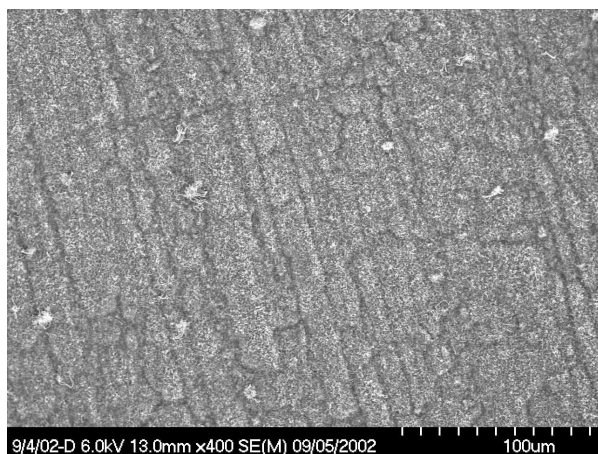


Figure 11. CNTs upon Cu foil to explore synergy with sensor contacts.

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13. ABSTRACT (Maximum 200 words) The objective of this research is to use a combination of carbon nanotubes and silicon-based microfabrication and micromachining processes to produce unique micro-sized chemical and gaseous sensors. Polished quartz substrate is used. Interdigitated structure is used for the sensing elements. Metallic catalysts for the growth of the carbon nanotube include copper, iron, nickel, and cobalt. Various thicknesses of the metallic catalysts are used in this study varying between 5 to 20 µm. Depositing of the metallic catalyst is accomplished using an ion-beam sputtering thin film technique and a shadow mask. Single wall carbon nanotubes are successfully formed over the metallic catalyst layer. Preliminary measurements of the carbon nanotubes show this nanotube contained film over the sensing elements which had a resistance value of 400 ohms at room temperature. This is a more conductive film comparing to metal oxide films, such as SnO ₂ or ZnO, that are now widely used in gaseous sensor research. Evaluation of the carbon nanotube film for potential gaseous sensing will be carried out.				
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